



doi:10.1016/j.gca.2003.07.023

Cycling of dissolved elemental mercury in Arctic Alaskan lakes

C. M. TSENG,^{1,*} C. LAMBORG,² W. F. FITZGERALD,² and D. R. ENGSTROM³¹National Center for Ocean Research, National Taiwan University, P.O. Box 23-13, Taipei, Taiwan, 106, ROC²Department of Marine Sciences, University of Connecticut, Groton, CT 06340, USA³St. Croix Watershed Research Station, Science Museum of Minnesota, St. Croix, MN 55455, USA

(Received May 15, 2002; accepted in revised form July 1, 2003)

Abstract—Aqueous production and water-air exchange of elemental mercury (Hg^0) are important features of the environmental cycling of Hg. We investigated Hg^0 cycling in ten Arctic Alaskan lakes that spanned a wide range in physicochemical characteristics. Dissolved gaseous Hg (DGM, dominated by Hg^0) varied from 40 to 430 fM and averaged 200 fM. All surface waters were supersaturated relative to the atmosphere. DGM averaged $3 \pm 2\%$ of dissolved (i.e., filter passing) dissolved total mercury (DTM) and $15 \pm 6\%$ of dissolved labile Hg (DLM). In-lake DGM profiles generally followed the vertical distribution of light, indicating photoreduction of Hg(II) complexes as a source of Hg^0 . Additionally, DGM correlated linearly with DLM ($r^2 = 0.82$, $p < 0.0001$) in the lake surface, signifying that Hg complexes (mostly organic Hg associations) in dissolved phase are photoreducible and contribute to production of DGM. Further, a positive relation between DGM/DTM and both K_a (light attenuation coefficient; $r^2 = 0.73$, $p < 0.02$) and DOC ($r^2 = 0.60$, $p = 0.02$) suggests that solar radiation and dissolved organic matter control DGM production and its cycling. An average rate of DGM formation ($0.6 \pm 0.2\%$ of DTM d^{-1} ; range, 0.20–0.8) was estimated by assuming steady state with the evasional rate. In-lake DGM formation occurs at lower rates in waters with greater suspended particulate matter and dissolved organic carbon (DOC), pointing to the significant role of organic matter plays in controlling DGM formation in these aquatic systems. Estimated evasional fluxes of Hg^0 (average, $140 \pm 50 \text{ pmol m}^{-2} \text{ d}^{-1}$; range, 60–200) were comparable to those of temperate lakes (e.g., Wisconsin, Michigan). In arctic lakes, the rate of evasion during ice-free periods ($7 \pm 3 \text{ nmol m}^{-2} \text{ yr}^{-1}$) is similar to the atmospheric input of Hg (wet + dry) to the lakes based on levels in summertime precipitation but not including additional sources, e.g., springtime depletion. Copyright © 2004 Elsevier Ltd

1. INTRODUCTION

Mercury (Hg) biogeochemistry in Arctic ecosystems, especially lakes, has received limited attention (Amyot et al., 1997a). Recently, additional interest in Hg deposition at high latitudes has been spurred by geochemical evidence for significant depletions in atmospheric levels of elemental Hg (Hg^0) during polar sunrise (Schroeder et al., 1998; Lindberg et al., 2000, 2002). Prior Arctic studies, though sparse, have reported that the high northern latitude regions are contaminated with Hg derived from human-related Hg emissions (Landers et al., 1995; Lockhart et al., 1995; Hermanson, 1998). Increasing deposition of Hg in the Arctic, related to long range atmospheric transmission and dispersion of Hg^0 , will enhance lake burdens of Hg. Therefore, the identification of the principal processes controlling air-water exchange and cycling of Hg, and assessment of their importance, is a pressing need.

Dissolved gaseous Hg (DGM) is composed primarily of Hg^0 , and its formation, distribution, and air-water exchange have been investigated in a variety of freshwater and marine environments (Fitzgerald et al., 1981, 1984, 1991, 1994; Kim and Fitzgerald, 1986; Vandal et al., 1991, 1995; Xiao et al., 1991; Mason et al., 1993a,b, 1994, 1995, 1999, 2001; Amyot et al., 1994, 1997a,b, 2000; Baeyens and Leemakers, 1998; Rolfhus, 1998; Costa and Liss, 1999, 2000; Lamborg et al., 1999; Fitzgerald et al., 2000; Poissant et al., 2000; Gårdfeldt et al., 2001; Rolfhus and Fitzgerald, 2001; Tseng et al., 2003a). These

studies have shown that dissolved Hg^0 measured as DGM can be produced in surface waters through biotic (bacteria and phytoplankton) and abiotic (photo-induced) processes, or by bacteria in light deficient waters. Such processes lead to supersaturation of volatile Hg^0 and subsequent evasion to the atmosphere across the water-air interface.

Field observations suggest that biologic reduction of Hg is related to phytoplankton and bacterial activities (Kim and Fitzgerald, 1986; Fitzgerald et al., 1991; Vandal et al., 1991; Mason et al., 1993a,b), and is supported by laboratory simulations and incubations (Ben-Bassat and Mayer, 1977, 1978; Barkay et al., 1989; Ji et al., 1989; Mason et al., 1995; Rolfhus, 1998). However, the mechanisms of biotic Hg reduction are not well understood.

Abiotic Hg^0 formation appears related principally to photolysis reactions in natural waters. Proposed mechanisms for Hg^0 formation include photochemical reactions involving dissolved organic matter (DOM) and/or Fe or Mn (Nriagu, 1994; Amyot et al., 1997b; Zhang and Lindberg, 2001). Humic and fulvic acids can reduce Hg(II) to Hg^0 in the laboratory (Alberts et al., 1974; Allard and Arsenie, 1991; Matthiessen, 1996). Direct and/or secondary photoreduction of Hg(II) complexed by DOM to Hg^0 was reported in lacustrine surface waters (Nriagu, 1994) and it was suggested that aqueous organic matter is probably involved in sunlight-induced reduction of Hg(II) complexes to Hg^0 . Presumably, given sufficient solar radiation, abiotic production of Hg^0 in aqueous systems can be enhanced as DOM increases.

Amyot et al. (1997a) conducted the first study of DGM cycling in Arctic lakes (74°N). They found sunlight-induced

* Author to whom correspondence should be addressed. (cmtseng@ncor.ntu.edu.tw).

Table 1. Limnological characteristics of the study lakes in Arctic Alaska.¹

Lake	Location	Type ²	A_W/A_L ³	Max. depth (m)	Area (ha)	Water volume (10^3 m^3)	T (C°)	pH	DOC ($\mu\text{M C}$)	SPM (mg L^{-1})	Cond ($\mu\text{S cm}^{-1}$)	DTM (pM)	K_a ⁴ Light (m^{-1})	K_a ⁴ UV _A (m^{-1})	K_a ⁴ UV _B (m^{-1})
12	68°34' N 149°33'E	D	16.1	18.0	8.4	685	12.9	8.0	483	0.1	24	8.9	0.74	4.4	10.9
14	68°35' N 149°34'E	D	49.4	8.0	8.7	275	13.4	8.0	475	2.0	21	6.4	0.81	4.3	10.6
15	68°36' N 149°35'E	D	34.0	8.4	18.1	679	13.1	8.1	450	0.2	23	6.6	0.67	4.0	9.6
16	68°37' N 149°36'E	D	56.4	15.8	16.7	1014	12.9	8.0	315	0.2	32	5.0	0.54	2.3	4.9
Toolik	68°38' N 149°38'E	D	44.9	25.0	149	10,566	11.8	7.9	353	0.7	48	8.5	0.67	2.7	6.1
Forgetful	68°53' N 150°17'E	H	2.3	12.4	7.4	265	12.3	8.1	360	0.9	50	6.7	0.75	2.8	6.3
Perfect	68°39' N 149°47'E	H	1.2	4.9	4.0	127	13.9	8.2	221	0.8	115	5.2	0.33	1.3	2.6
Efficient	68°42' N 149°42'E	H	4.5	13.0	4.0	188	13.7	8.3	256	0.1	194	5.7	0.42	1.7	3.4
Surprise	68°32' N 149°39'E	H	3.0	6.3	2.5	67	13.0	8.0	249	1.2	144	5.7	0.40	1.6	3.2
Relaxing	68°44' N 150°02'E	H	2.9	12.4	6.0	294	14.8	8.0	356	0.2	88	6.0	0.49	2.8	6.2

¹ T, pH, DOC, suspended particulate matter (SPM), conductivity (Cond) and dissolved total mercury (DTM) are for the epilimnion; morphometric data for Toolik and I-series lakes from Kling *et al.* (2000).

² D denotes drainage lakes (those with inlet and outlet streams); H represents headwater lakes (without inlet streams).

³ Ratio of watershed to lake area.

⁴ K_a light, K_a UV_A and K_a UV_B represent the estimated attenuation coefficients for downward irradiance of the visible light, UV_A, and UV_B, respectively. Calculated equations: K_a UV_A = $0.299 \times (\text{DOC})^{1.53}$; K_a UV_B = $0.415 \times (\text{DOC})^{1.86}$, where DOC is in mg L^{-1} (Scully and Lean, 1994). K_a light calculated from $I_z = I_0 \times e^{-K_a z}$, where I_0 and I_z = light density at subsurface and depth Z (in meters), respectively.

reduction promotes DGM formation and that the rate of DGM production was positively related to the intensity of solar radiation; the highest levels and formation rates for DGM were found in surface waters of lakes. In addition, the availability of photoreducible Hg(II) complexes was identified as a limiting factor affecting the rate of DGM production. These findings further support the “Hg(II) substrate hypothesis” proposed by Fitzgerald *et al.* (1991), in which environmentally important Hg reactions such as reduction and methylation were hypothesized to be controlled by the availability of inorganic Hg species (i.e., reactant).

Here, we report results from our investigations on the production, behavior, and fate of DGM in Arctic lacustrine systems conducted during July 2000 as a part of our broadly based examination of Hg contamination and cycling in the tundra regions of northeastern Alaska. The goals of this study were to test the following hypotheses: 1) In situ production and evasion of DGM will be favored in the near surface photoactive zone, and the rate of DGM production will be related to the distributions of the labile (reactive) Hg and that of reducing agents (e.g., DOM); and 2) oligotrophic Arctic lakes have significant evasional losses of Hg as Hg⁰ during the ice-free season and these emissions are enhanced by an increased photo-reduction period associated with 24 h of daylight during the summer. The experimental approach was designed to provide a comprehensive test of the hypotheses and a broader understanding of the aqueous biogeochemistry of Hg. Thus, we selected ten lakes that displayed a representative range of limnological and physicochemical properties (Table 1). Dissolved and particulate Hg species were measured in each lake along with factors posited to regulate the formation and the distribution of DGM in lake waters [e.g., solar radiation (S_R), dissolved organic carbon (DOC), and suspended particulate matter (SPM)]. Based on prior work (Rolfhus, 1998; Rolfhus and Fitzgerald, 2001), we focused on the interaction between Hg and aqueous organic matter as it relates to the control of labile Hg, the substrate for DGM production, in sunlight. We quantified Hg⁰ evasional fluxes and evaluated their importance relative to the atmo-

spheric Hg deposition (i.e., wet and dry deposition). We compared the Hg species distribution for inflows, and outflows with in-lake patterns to assess the relative roles of in-lake cycling and stream inputs in affecting in situ DGM production and evasion. Finally, we estimated in-lake formation rates of DGM and evaluated the influence of the various chemical (e.g., DOC, SPM) and physical parameters (e.g., solar radiation, water temperature) on rates of DGM production.

2. MATERIALS AND METHODS

2.1. Study Site

We examined DGM in ten lakes located in the tundra of Alaska's North Slope, surrounding the Long Term Ecological Research (LTER) site at the Toolik Field Station (68°38'N, 149°38'W). All lakes were formed by glaciation ~10,000–12,000 yr ago and lay mainly in a glacial outwash valley (Brown and Kreig, 1983). The study lakes ranged from small headwater systems to lakes with large watershed/lake area ratios (A_W/A_L). The A_W/A_L variation is a useful normalizing framework for evaluating the influence of atmospheric and watershed inputs on Hg cycling (Swain *et al.*, 1992). Five of these, the “I-series” lakes (I-2, I-4, I-5, I-6) and Toolik Lake, have large A_W/A_L ratios (20–60) and drain sequentially into each other through surface streams, which eventually flow into the southeastern part of Toolik Lake (Fig. 1). The other five lakes are characterized as headwater lakes with small A_W/A_L ratios (1–5). These “headwater lakes” are remote and far from any direct human-related influences (e.g., road runoff or population effects). The “I-series” lakes and Toolik are located within a few kilometers of the traveled Dalton Highway.

Basic hydrographic parameters for the ten study lakes are listed in Table 1 and shown in Figure 2a. Lakes in the Arctic North Slope have a short ice-free season, ranging between mid to late June and late September, with July water temperatures that are usually <15°C. They are characterized as oligotrophic (Hobbie, 1984; Miller *et al.*, 1986). North Slope lakes, how-

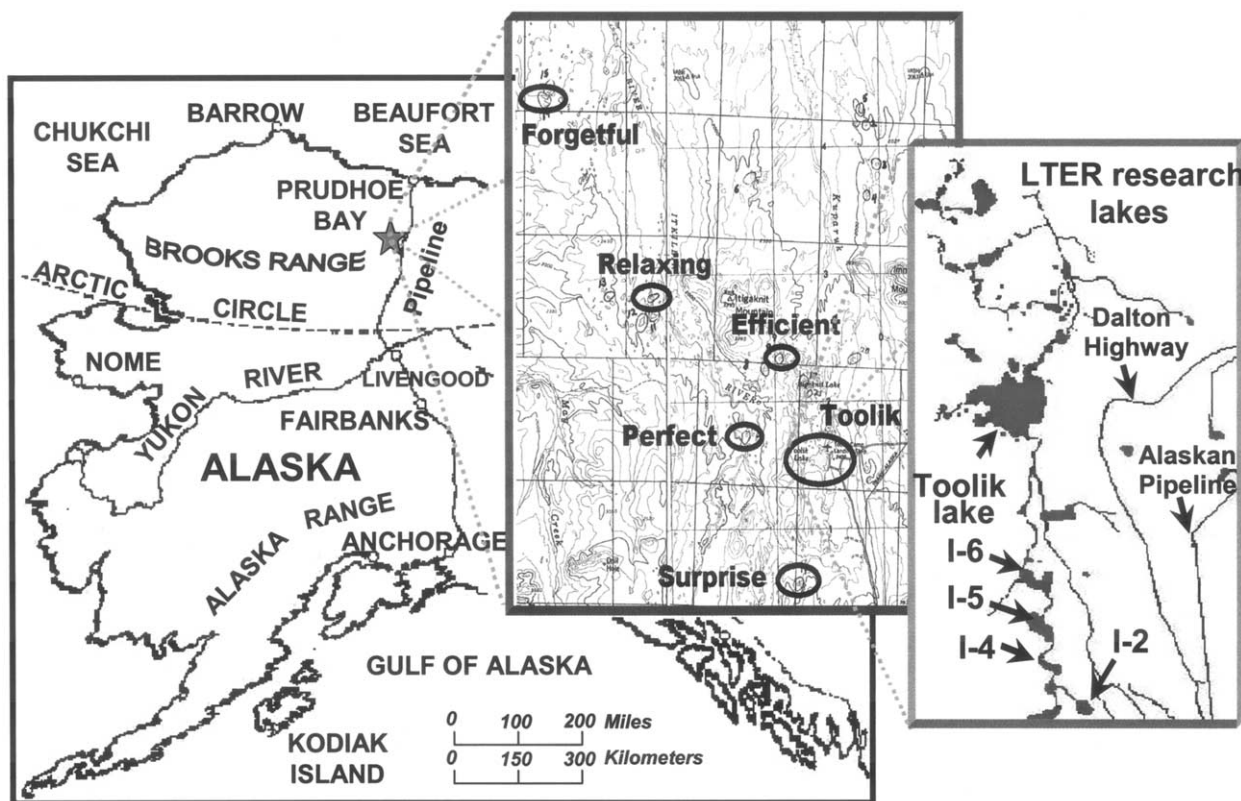


Fig. 1. Location of the 10 study lakes (stars) in northeastern Alaska, USA.

ever, contain relatively high levels of DOC (200–1000 $\mu\text{M C}$; Kling et al., 2000), which are principally derived through leaching from the tundra drainage basin with the covers of different vegetation (e.g., a myriad of mosses, lichens and other vegetation). The water chemistries of tundra lakes vary with localities due to differences in bedrock, the age of associated glacial drift and eolian material input (Kling et al., 1992).

2.2. Sample Collection and Processing

On-site investigations were conducted during July 10–24, 2000. Ultraclean trace metal techniques and protocols were followed during the sample collection and analysis (Gill and Fitzgerald, 1985; Vandal et al., 1991; Mason et al., 1993a,b; Fitzgerald, 1999). Lake surface waters were sampled from a rubber boat by hand-dipping acid-cleaned 2-L Teflon bottles from the front of the boat while moving forward into the wind. Vertical profile samples were collected with an 8-L Teflon-coated Go-Flo bottle (General Oceanics, USA) suspended on Kevlar line. This Go-Flo bottle was precleaned with 10% nitric acid and blank tests were performed before field sampling to check for potential contamination.

Seven of the study lakes had thermoclines, and water was sampled from both the epilimnion and hypolimnion. Only surface samples were collected from the other three lakes. Samples collected with the Go-Flo bottle were immediately transferred into acid-cleaned 2-L Teflon bottles, which were double-bagged and transported in coolers to the laboratory at

Toolik Lake. DGM analysis was performed on the day of collection.

DOC, pH and SPM also were measured in subsamples obtained from the Go-Flo bottle during each cast. Dissolved and particulate material were separated by filtration through a pre-cleaned and preweighed 0.45- μm polycarbonate filter using a pressurized (2 bar N_2), Teflon-lined, pneumatic filtration system (Tseng et al., 2001). DOC and Hg species concentrations were determined in the filtrate. DOC was measured at the St. Croix Watershed Research Station using a Dohrmann Phoenix 8000 UV persulfate carbon analyzer (Tekmar-Dohrmann, Cincinnati, OH). The loaded polycarbonate filters were dried inside of a laminar flow hood at room temperature for Hg analysis and SPM determination. Conductivity, dissolved O_2 and temperature were measured in situ during each sample collection with a CTD probe (Yellow Springs Instrument Co.), and vertical profiles of Photosynthetically Active Radiation (PAR, wavelengths 400 to 700 nm) were determined with a LI-193SA underwater radiation sensor (LI-COR).

2.3. DGM Determination

DGM is defined operationally as the Hg^0 collected on a gold (Au) trap after purging an unamended sample with N_2 gas (Vandal et al., 1991; Mason et al., 1993a,b). Briefly, a 2-L sample is purged with Hg-free N_2 in a 2.5-L borosilicate bubbler and the Hg is amalgamated onto a gold-coated trap. Analyses are conducted by pyrolysis in a two-stage Au amal-

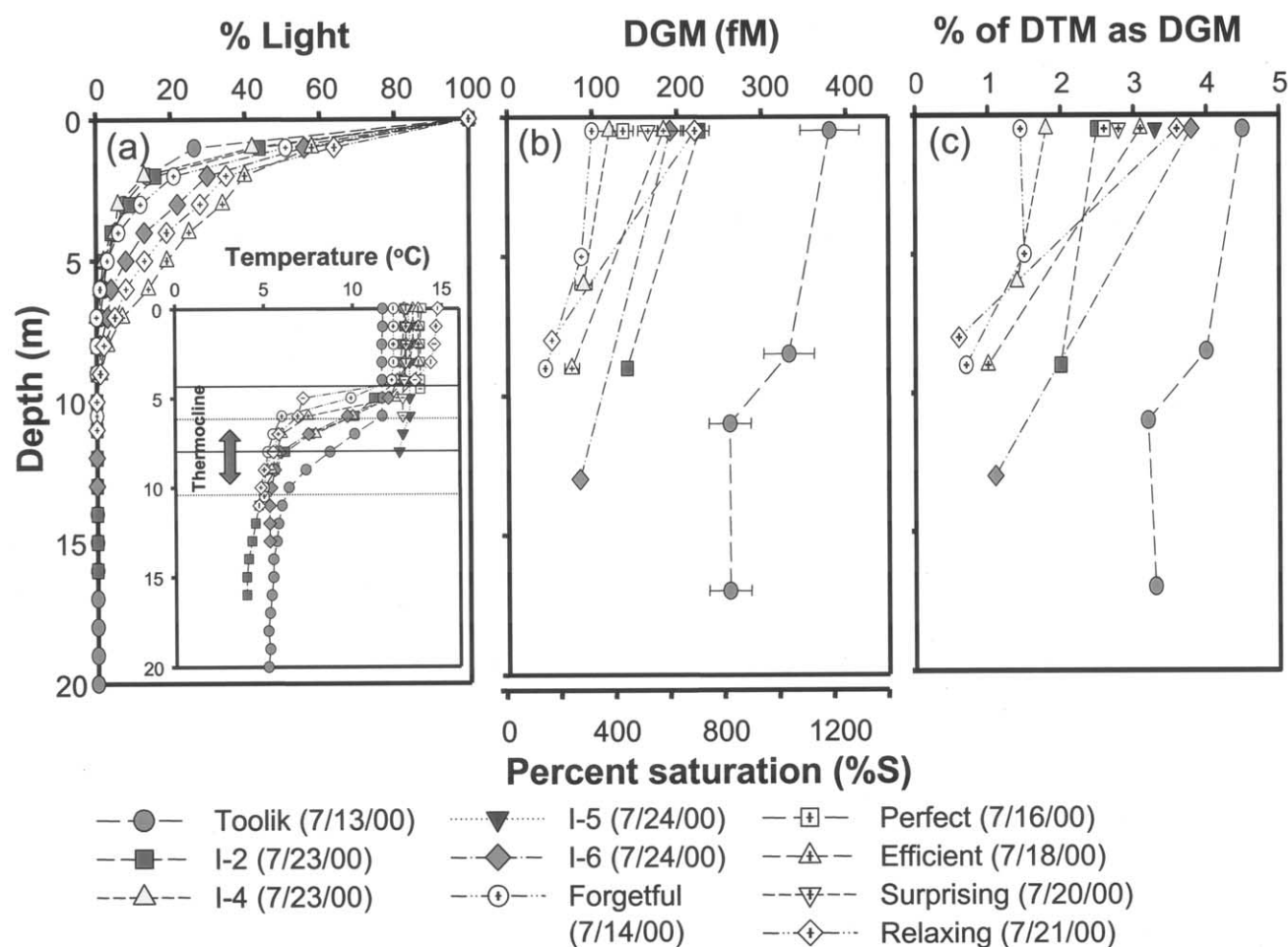


Fig. 2. Depth profiles of DGM and its information related to concentration, saturation degree and percent DGM and hydrography and in the study lakes. Sampling dates are given in parentheses and errors are ± 1 SD.

gamation gas train with detection by atomic fluorescence spectroscopy (AFS; Fitzgerald and Gill, 1979; Bloom and Fitzgerald, 1988).

In this study, we used a novel semiautomatic in-line purge-and-trap system, coupling the two-stage Au-amalgamation and flow-injection techniques with AFS (Tseng et al., 2003). This analytical framework provides simple, rapid, precise, and accurate analyses. Complete trapping of DGM for a 2-L water sample can be achieved with a 30-min purge at a $1 \text{ L min}^{-1} \text{ N}_2$ flow rate. Instrument calibration was performed by injection of known masses of a Hg^0 gas standard into both the Ar gas stream (before sample or analytical traps) and the bubbler. Hg^0 averaged $15 \pm 2 \text{ pg}$ in procedural blanks (mean ± 1 SD, $n = 10$) during the 3-week measurement period. Method detection limit (MDL) for DGM analysis, defined as 3σ of procedural blanks, was $\sim 30 \text{ fM}$. The relative standard deviation of replicate DGM samples, a measure of overall precision, was less than 10% ($n = 3$). Recovery from analytical spikes averaged $100 \pm 5\%$ ($n = 30$).

Mercury species other than DGM also were measured in lake waters, including filter-passing dissolved Hg species such as dissolved labile Hg (DLM) and dissolved total Hg (DTM), and particulate inorganic Hg (PIM). DLM is defined operationally

as the Hg in $<0.45 \text{ }\mu\text{m}$ -filtered aliquots that is reduced by SnCl_2 at natural pH levels. This fraction includes inorganic complexes and kinetically labile organic associations in truly dissolved and colloidal phases (Lamborg et al., 2003). PIM was determined by the difference between particulate total Hg (PTM) in samples digested with 1:1 HCl:HNO_3 (Tseng et al., 2001) and particulate organo-Hg species (i.e., monomethylHg) extracted with 2 N HNO_3 (Tseng et al., 1997). DTM is determined after chemical digestion with BrCl , followed by $\text{NH}_2\text{OH}\cdot\text{HCl}$ prereduction and SnCl_2 reduction. All speciation measurements were made with the SnCl_2 reduction/Au amalgamation technique with cold-vapor AFS detection (Bloom and Crecelius, 1983; Bloom, 1994). We reduced sample handling by connecting the reduction, purging, trapping, desorption and detection mechanisms in-line with hand-operated valves. This set-up is similar to that described for DGM analysis so that high quality analytical performance can be easily achieved.

2.4. Light Attenuation Determination

Water column light attenuation of each lake was evaluated as the attenuation coefficient (K_a , m^{-1}) for downward irradiance of PAR. K_a was determined from the slope of a linear regres-

sion of $\ln(I_z/I_0)$ versus depth, assuming light extinction follows $I_z = I_0 \times \exp(-K_a Z)$, and I_0 and I_z are respective irradiances at the surface and at depth Z (in meters).

2.5. Percent Saturation

Percent saturation (%S) of Hg^0 with respect to atmospheric equilibrium was determined with the following equation:

$$\%S = [(DGM \times H)/H_g^0] \times 100 \quad (1)$$

where DGM and H_g^0 are the concentrations measured in surface water and in the overlying air, respectively. H is the temperature-dependent Henry's Law constant for Hg^0 (Sanemasa, 1975). The values of H in this study were in the range of $290\text{--}310 \text{ atm (mole fraction)}^{-1}$ at the water temperatures of $11\text{--}15^\circ\text{C}$. Values of $\%S > 100$ indicate supersaturation and the potential for evasion of Hg at the water-air interface.

2.6. Flux Calculation

In this study, flux estimates for air-water gas exchange of Hg^0 were made using the thin film gas exchange model in which the Hg^0 flux is assumed proportional to the air-water concentration gradient (Liss and Slater, 1974; Vandal et al., 1991). The flux is expressed as:

$$F = K \times (DGM - H_g^0/H) \quad (2)$$

where F is the volatile Hg^0 flux into (−) or out (+) of the lake and K is the transfer velocity at the air-water interface. K for Hg^0 can be estimated from the model of Wanninkhof et al. (1985) for use on small wind-fetch lakes:

$$K = 0.45 \times u_{10}^{1.64} \times (Sc_{Hg}^T/600)^{-0.5} \quad (3)$$

where Sc_{Hg}^T is the Schmidt number for Hg^0 (ranging from 490–610 in these lakes) and u_{10} is the wind speed (m s^{-1}) measured at a height of 10 m. The wind speed exponent (1.64) and coefficient (0.45) values were obtained empirically from SF_6 tracer experiments and provide a K value with units of cm h^{-1} .

3. RESULTS AND DISCUSSION

3.1. DGM Distribution

Volatile Hg was found mainly as Hg^0 in air and natural waters. Accordingly, DGM in the study lakes was assumed to be principally Hg^0 (>99%), as found in Canadian Arctic lakes (Amyot et al., 1997a). The data in vertical profiles of DGM and information related to concentration, saturation degree and percent DGM and hydrography (e.g., temperature, light penetration) in the study lakes are shown in Figure 2. With the exception of Toolik Lake, the levels and distribution of DGM were similar among the study lakes (Fig. 2b). All the samples were supersaturated with DGM (ca. 110–1300%) relative to atmospheric equilibrium. Surface DGM concentrations ranged from 100 to 230 fM (i.e., 10^{-15} M), while percent saturation (%S) ranged from 300 to 800%. The average surface concentration was 180 fM, representing an average %S of $600 \pm 200\%$ (mean $\pm 1 \text{ SD}$, $n = 9$). Of the ten lakes sampled, Toolik Lake had the highest DGM levels in surface waters (average,

380 fM, $n = 5$; range, 350 to 430 fM) with percent saturation levels up to 1300% at the surface.

Site specific in-lake DGM for Toolik showed only slight temporal variability on short timescales. For example, surface concentrations of DGM at sites within Toolik Lake were $430 \pm 50 \text{ fM}$ on July 11 and $370 \pm 30 \text{ fM}$ 2 d later, and were therefore statistically indistinguishable. Levels of DLM and DTM, which appear to show a slightly larger magnitude of variation, were $3.0 \pm 0.3 \text{ pM}$ (i.e., 10^{-12} M) and $11.2 \pm 0.6 \text{ pM}$ on July 11 and 2.1 ± 0.2 and 8.2 ± 0.5 on July 13, respectively.

Vertical profiles of DGM and %S decreased with depth (Fig. 2b). Concentrations and %S of DGM were greatest in the epilimnion and were 2–6 times greater than levels in the hypolimnion for all the lakes. Similar observations of decreasing DGM with depth were observed in temperate lakes (Vandal et al., 1991; Amyot et al., 1994, 1997b) and Arctic lakes (Amyot et al., 1997a). DTM in our lakes varied significantly among the lakes with a range of 4–10 pM (surface DTM shown in the Table 1). The fraction of DTM as DGM was 3–5% in Toolik Lake. This was two times greater than that found in the other nine study lakes, which averaged $2 \pm 1\%$ (Fig. 2c).

3.2. Factors Affecting DGM Distribution and Formation

3.2.1. Effect of Sunlight

In-lake DGM and % of DTM as DGM profiles, in general, decreased with increasing depth (Fig. 2), suggesting photochemical production, as found for Arctic lakes by others (Amyot et al., 1997a). Additionally, we observed, in this study, that aqueous light transmission varied significantly among lakes. The variation in PAR light attenuation, evaluated as the attenuation coefficient (K_a , m^{-1}), depended primarily on DOC (Fig. 3a). K_a was positively related to DOC in surface waters of the study lakes (Fig. 3a). This relationship has also been observed in temperate lakes (e.g., Scully and Lean, 1994; Morris et al., 1995). The connection between light attenuation and DOC is the result of the chromophoric properties of DOC compounds, including humic acids (HA), fulvic acids (FA), protein amino acids and porphyrin derivatives (Larson and Marley, 1994). It is evident from Figure 3a ($r^2 = 0.82$) that factors other than DOC, such as SPM and POC, contributed less than 20% of the variability in light absorption in these lakes. The range of the light extinction coefficients in our study lakes was from 0.4 to 0.9 m^{-1} , similar to those reported for other Arctic lakes (Hobbie, 1973).

The distribution of DGM in surface waters was related, in part, to changes in K_a among lakes ($r^2 = 0.50$, $p = 0.02$, data not shown). DGM levels increased with increasing K_a in the range of 0.3 and 0.6 m^{-1} . After the maximum, DGM decreased with increasing K_a . The relation between DGM/DTM and K_a was even more pronounced in Figure 3b ($r^2 = 0.73$, $p < 0.02$, quadratic function). The trend, which peaks at about $K_a = 0.6 \text{ m}^{-1}$, appears exactly like that for the fraction of DGM/DTM versus DOC (section 3.2.3), implying that the relative importance of solar radiation on Hg photoreduction processes is related to the amount and type of organic matter (i.e., as reducing agents) present in the water column. The extinction coefficients for UV_A (280–320 nm) and UV_B (320–400 nm) in the study lakes, estimated from DOC concentrations (Scully

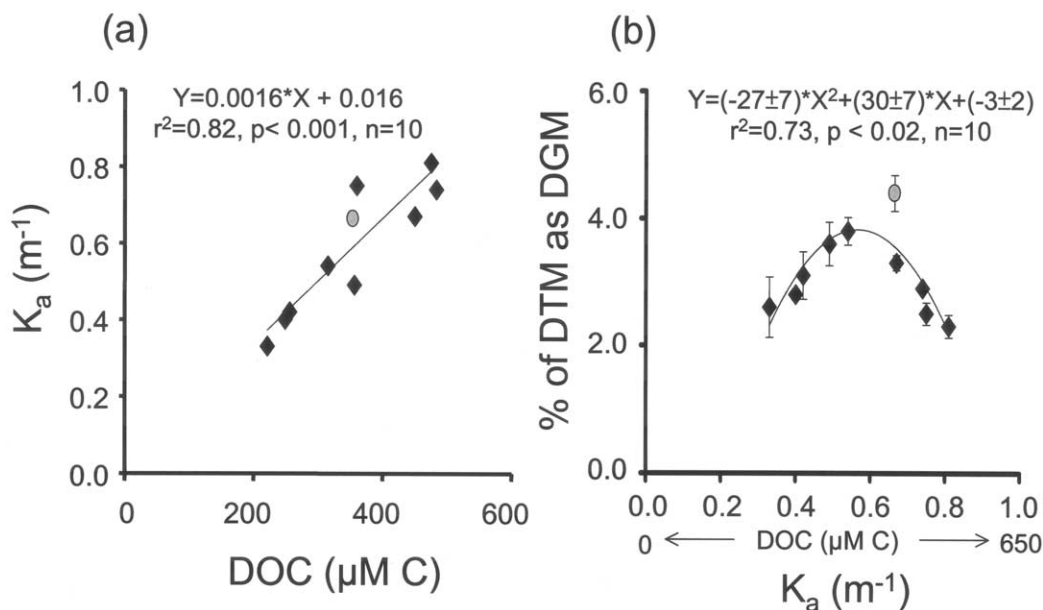


Fig. 3. Relationships between (a) K_a (light attenuation coefficient) and DOC; and (b) fraction of DTM as DGM and K_a (or DOC) in the study lakes. Sample "Oval" from Toolik Lake; "diamond" from other nine lakes. Errors are ± 1 SD.

and Lean, 1994), were much greater than that for PAR (Table 1), indicating only shallow UV penetration (e.g., on average, UV_B decreased to 1% at 1 m). Thus, while the effects of UV_A and UV_B on Hg photoreduction could be significant, they are confined to a shallow photoactive zone in these relatively high DOC lakes. When the fraction of DGM/DTM is plotted against UV_A (and UV_B), results similar to those in Figure 3b are observed. These relationships are comparable to those found in Canadian Arctic lakes (Amyot et al., 1997a) and seawater (Costa and Liss, 2000).

3.2.2. Effect of Hg Speciation

As shown in Figure 4a, in the surface waters of the study lakes, DGM was positively correlated related with DLM (Slope = 0.170 ± 0.02 , unitless; $r^2 = 0.82$, $p < 0.0001$). That is, greater DGM concentrations were observed as Sn(II)-reducible Hg levels increased. The strong correlation implies that the concentrations of photoreducible Hg substrates govern DGM formation and distribution. Thus, the results from the current investigation were apparently consistent with the "Hg(II) substrate hypothesis."

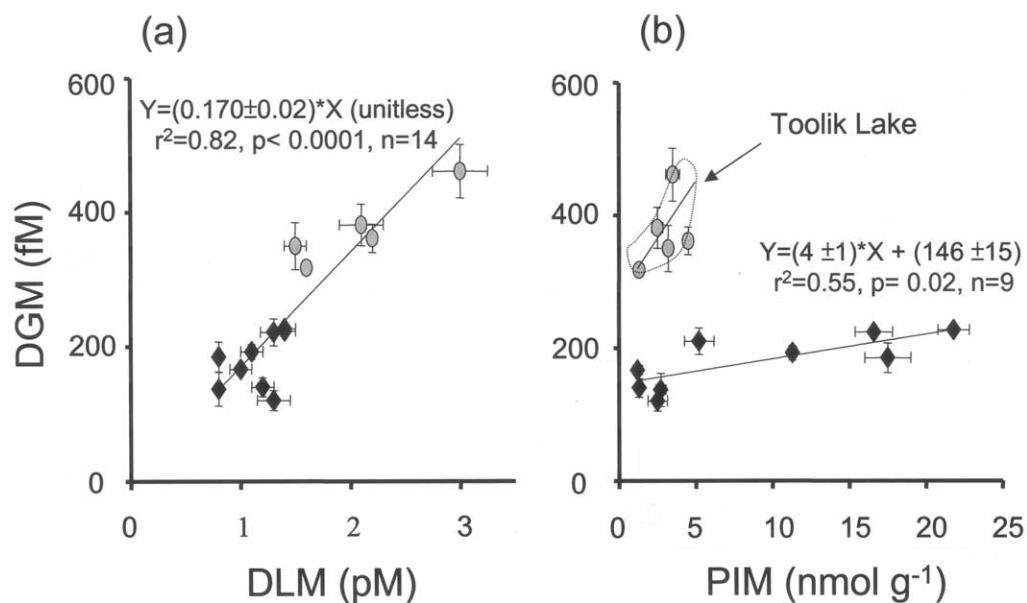


Fig. 4. Relation between DGM and both (a) DLM and (b) PIM for the study lakes. Sample "Oval" from Toolik Lake; "diamond" from other nine lakes. Errors are ± 1 SD.

We note, however, that while a good correlation was evident between DGM and DLM, the reactant or substrate is operationally-defined (Bloom, 1994). The Sn(II)-reducible Hg is a mixture of species, Hg(II) and organic Hg complexes. The extent of inorganic and organic Hg complexes extracted depends on the analytical conditions (e.g., acid concentration, storage, and analysis time) as well as the composition of the aqueous media (e.g., freshwater or seawater). Although the Sn-reduction determination of labile Hg has been used to provide a measure of the pool of Hg available for reduction in natural waters, it does not provide accurate information on inorganic/organic partitioning nor does it address the potential for reduction of Hg associated with particulate matter.

It is likely that certain particulate labile Hg species could be reduced via either abiotic or biotic processes or both. This potential source of substrate was evident by the moderate linear correlation between DGM and PIM (Fig. 4b; Slope = $4 \pm 1 \mu\text{g L}^{-1}$, intercept = $146 \pm 15 \text{ fM}$, $r^2 = 0.55$, $p = 0.02$, $n = 9$). Particulate matter in oxic Arctic lake waters are composed mainly of colored organic matter aggregates and Fe/Mn oxides (we observed the filtered particulates to vary in color from the light brown/red to dark red). Organically associated Fe/Mn oxides can absorb light and be photolytically reduced, generating reducing equivalents that may react with Hg(II) (Stromberg et al., 1991). Also, these photoactive particles, exhibiting semiconducting properties, may serve as direct Hg reducing agents in the presence of light (Nriagu, 1994). As illustrated in Figure 4b, DGM in Toolik Lake did not show a direct correlation with PIM. However, this was likely due to the small range in both DGM and PIM. Thus, in summary, the particulate pool appears to contribute to DGM production but its contribution is minor ($\ll 20\%$ of total DGM production) relative to dissolved Hg. Indeed, most of the Hg was in the dissolved phase ($\sim 80\%$ of total Hg) and the slope from regression line (Fig. 4b) is quite small. This indicates that only a very small portion of particulate Hg pool was involved in Hg photoreduction.

3.2.3. Effects of Dissolved Organic Matter

In fresh waters, estimates of conditional formation constants ($\log K'$) for Hg-humic complexes range from 17–23 (Mantoura et al., 1978; Dyrssen and Wedborg, 1991; Benoit et al., 2001). Preliminary data suggest similar results for these lakes (Lamborg et al., 2003). Given the low Cl ($\sim 10 \mu\text{M}$), high pH (7.1–8.4), large stability constants (average $\log K' = 22.5$) and ligand concentrations (on the order of 10 nM), nearly all of the Hg(II) should have been organically associated ($>99\%$ of total Hg). In temperate lakes, several reports show that DGM production was positively related to lake pH (Vandal et al., 1991; Fitzgerald et al., 1994). This increase was attributed to a pH related enhancement in the fraction of Hg(II) present as a Hg hydroxyl species, $\text{Hg}(\text{OH})_2^0$. Since our study lakes did not display a large pH range, a pH effect could not be assessed in this work. The effect of pH on speciation is not expected to be significant, however, and Hg should always be present as an organic complex in lakes of typical DOC concentration. It is possible that the pH effect observed in some lake systems was the result of changes in the amount and type of organic matter present, as organic matter can control lake pH.

The potential influences of DOC on aqueous DGM formation in surface waters are seen in Figure 3b, where K_a can be viewed as a proxy of DOC. The fraction of DGM increased with increasing DOC up to $\sim 400 \mu\text{M}$, and thereafter the %DGM decreased. These results are consistent with those obtained from laboratory experiments concerning rates of DGM formation under variable DOC regimes (Rolfhus, 1998; Costa and Liss, 2000). The importance of Hg-organic complexes as the substrate for DGM production can be illustrated by assuming the curve in Figure 3b can be extrapolated to the zero DOC intercept (i.e., K_a approaching zero). If this is done, Figure 3b predicts that little DGM would be formed when there is no DOC for complexation and the dominant Hg species is $\text{Hg}(\text{OH})_2^0$. Furthermore, the nonlinear relationship in Figure 3b, whereby %DGM increases with DOC to an optimum level beyond which increases in DOC appear to inhibit the formation of DGM, suggests the following competing processes:

- 1) Assuming that Hg must be complexed by organic ligands of some kind, below the optimum DOC concentration, increases in DOC result in increased complexation of Hg by organic ligands. Such Hg-organic complexes provide a substrate for photochemically induced redox reactions yielding Hg^0 and oxidized organic molecules. This increasing trend continues until, at the optimum DOC concentration, all the Hg present is complexed with the photoactive component of the DOC pool.

- 2) Beyond the optimum DOC concentration (the equivalence point), further increases in light-absorbing DOC serve only to lower the number of photons reaching Hg-DOC complexes and thereby lower the Hg specific reduction rate.

The overall mechanism outlined above is different than the conventional view of photoreduction of Hg(II) via photolysis of dissolved Hg(II)-complexes induced indirectly by receiving electrons from photoactivated species (Nriagu, 1994; Stumm and Morgan, 1995) such as Fe and Mn (Nriagu, 1994; Zhang and Lindberg, 2001) and transient species (e.g., $\text{O}_2^{\bullet-}$, H_2O_2 , organic radicals; Schroeder et al., 1992; Xiao et al., 1995; Pehkonen and Lin, 1998; Zhang and Lindberg, 2001). If the indirect photoreduction mechanism were dominant, release of Hg from organic complexes would be the rate limiting step, as the photolysis rate for Hg is expected to be fast (Brosset and Lord, 1991; Munthe et al., 1991). The organic complex release rate would have to be similar to the rate of reduction ($\sim 0.3\%$ to 0.8% of DTM d^{-1} , see the following section), to sustain steady state. This release rate would be dependent on the amount and nature of DOM. Lamborg et al. (2003) found the rate of organic complex release is generally slower than typical rates of reduction.

In the alternative mechanism, organic complexes-Hg are reduced directly by electrons provided by the photoreduction of chromophoric dissolved organic matter (CDOM). Thus, the donor and Hg(II) form a charge-transfer complex and the electron transfer occurs within the light-sensitized organic complexes (Nriagu, 1994). The Hg specific rate of reduction by this pathway would be a function of CDOM complexation properties (and thereby the extent of Hg complexation), light attenuation by excess organic matter and the electronic characteristics of the Hg-organic matter complex.

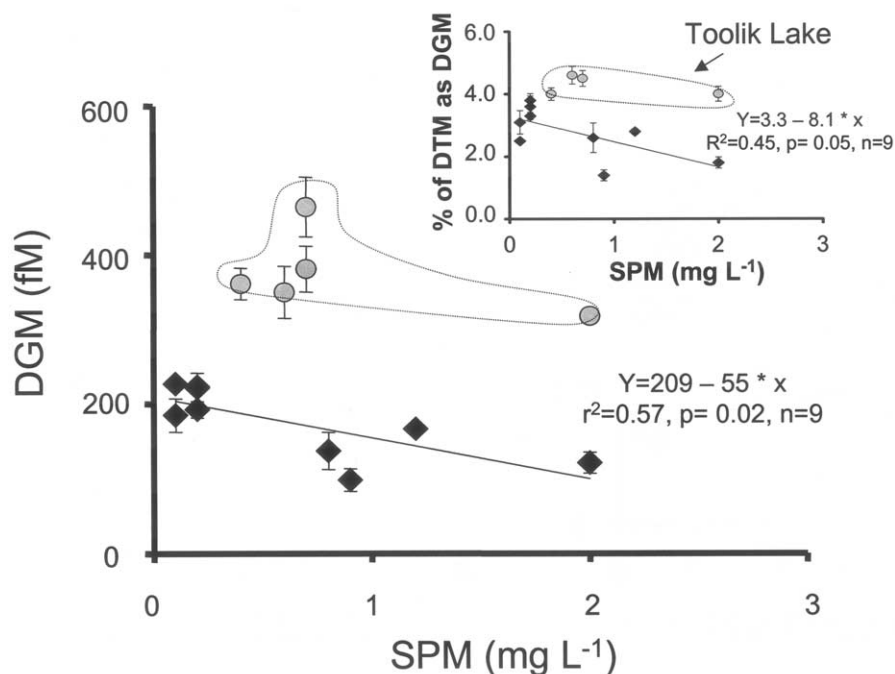


Fig. 5. Relationships between DGM (and percentage of DTM as DGM) and suspended particulate matter (SPM). Sample "Oval" from Toolik Lake; "diamond" from other nine lakes. Errors are ± 1 SD.

3.2.4. Effect of Suspended Particulate Matter

Figure 5 shows the inverse relationship between DGM (both in concentration and in % of DTM as DGM) and the SPM concentration in surface waters of lakes. Lower DGM levels were observed in surface waters with higher SPM concentrations. Toolik Lake, which had comparatively greater levels of DGM, lies on a similar trend. Thus, SPM appeared to have some effect on the control of DGM concentrations. Such an effect on DGM production is possibly explained by 1) decreases in labile particulate Hg complexes as SPM increases, and 2) the removal of reactant by coprecipitation/adsorption on mineral surfaces and organic coatings (Tseng et al., 2001). Such scavenging processes compete with reduction and the subsequent evasion of Hg. Alternatively, particulate material, derived from watershed inputs or sediment suspension, may enhance the rate of Hg⁰ oxidation in natural waters.

3.3. In-Lake DGM Production

As mentioned previously, the greatest level of DGM supersaturation in the lakes was observed in the epilimnion. Additionally, for Toolik Lake, in-lake DGM production was indicated clearly by differences in Hg⁰ for the inflow ($n = 2$) and outflow ($n = 2$) (Table 2). Levels of DGM were lowest in the stream entering Toolik Lake, having DGM concentrations similar to equilibrium with the atmosphere (ca. 40 fM, near our detection limit). In contrast, the outflow contained 10 times as much as DGM as the inflow. This distribution is consistent with the enhanced gas exchange expected for tributaries that are shallow and highly turbulent. Thus, the major cause of in-lake supersaturation of DGM was in situ production. Arctic lakes can be thought of as an incubator for the processing of Hg (i.e., in-situ DGM production and evasion) delivered from the atmosphere and watersheds.

Table 2. Mercury species in Toolik Lake and its inflow and outflow waters.

Sampling date	Location	n ³	Dissolved Hg species in surface waters				
			DGM			DLM (pM)	DTM (pM)
			fM	% DGM/DTM ¹	%S ²		
07/10/2000	Inflow	2	35 \pm 2	0.4 \pm 0.1	110 \pm 10	2.4 \pm 0.2	9.1 \pm 0.1
07/11–13/2000	In-lake	5	380 \pm 50	4.3 \pm 0.3	1100 \pm 200	2.3 \pm 0.5	8.5 \pm 1.6
07/12/2000	Outflow	2	330 \pm 30	4.3 \pm 0.2	1000 \pm 100	1.8 \pm 0.4	7.5 \pm 0.5

¹ Percentage of DTM as DGM.

² Percent saturation (%S) for DGM in the water relative to appropriate temperature corrected equilibrium with atmospheric Hg⁰.

³ Numbers of samples analyzed.

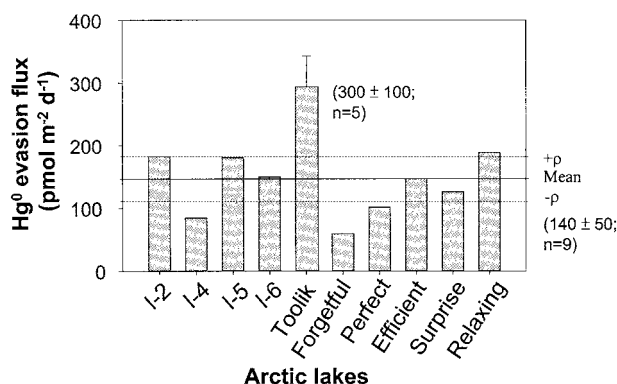


Fig. 6. Evasion fluxes of Hg^0 on average (mean \pm 1 SD, sample numbers) from the study lakes. Fluxes are estimated with the following conditions: $u_{10} = 3.7 \text{ m s}^{-1}$, $T_v = 0.9 \text{ m d}^{-1}$, Hg^0 concentration in the air and water with atmosphere equilibrium are 7.5 pmol m^{-3} and 35 fM , respectively. In situ surface water temperature ranged from 11 to 15°C during the summer season in July 2000.

3.4. Hg Fluxes to the Atmosphere

Evasion fluxes of Hg^0 were estimated with Eqns. 2 and 3 for lake waters, as mentioned above. Surface water temperatures, measured in situ, ranged from 11 to 15°C , and wind speed (u_{10}), measured at Toolik field station averaged 3.65 m s^{-1} in July 2000. The time-weighted air concentration of Hg^0 measured at Toolik during the survey was $1.5 \pm 0.2 \text{ ng m}^{-3}$. The mean transfer velocity obtained using Eqn. 3 was $\sim 0.9 \text{ m d}^{-1}$. The evasional flux, calculated by using the average transfer velocity in July 2000, provides a general estimate for comparison with other significant fluxes. The uncertainty of the evasion flux calculation is $\sim 30\text{--}40\%$ (Rolfhus and Fitzgerald, 2001), and is strongly related to the evaluation of transfer velocity.

The estimated Hg^0 emissions from the studied lakes, except Toolik, ranged from $60\text{--}190 \text{ pmol m}^{-2} \text{ d}^{-1}$ with a mean of 140 ± 50 (± 1 SD; Fig. 6, Toolik Lake averaged $300 \pm 100 \text{ pmol m}^{-2} \text{ d}^{-1}$). This range of fluxes for Arctic Alaskan lakes is comparable to those of temperate lakes in Wisconsin ($50\text{--}270 \text{ pmol m}^{-2} \text{ d}^{-1}$, Vandal et al., 1991), Ontario, Canada ($5\text{--}155 \text{ pmol m}^{-2} \text{ d}^{-1}$, Amyot et al., 1997b; median $90\text{--}230$, Poissant et al., 2000) and Lake Michigan ($120 \pm 70 \text{ pmol m}^{-2} \text{ d}^{-1}$, Mason and Sullivan, 1997). However, these Hg^0 emissions estimates are greater than those reported for lakes studied by Amyot et al. (1997a) in the Canadian Arctic.

The annual Hg^0 flux can be estimated conservatively by assuming that the conditions observed during July apply to the warmest lake water period (i.e., July and August or ca. 50 d). The ice-free period for this Arctic region lasts ~ 3 months (late June to late September). Moreover, the long-term data for Toolik Lake indicates that the mean water temperature is less than 5°C in June and September. Estimated DGM levels for these cold temperatures and lower light irradiation conditions are expected to be low and near atmospheric equilibrium (Vandal et al., 1991; Xiao et al., 1991). This expectation is based on the temperature dependence of DGM formation (following section). Accordingly, Hg^0 fluxes to the atmosphere ($<0.5 \text{ nmol m}^{-2} \text{ month}^{-1}$) should be small ($<5\%$) relative to those in July and August.

Annualized lacustrine Hg mass balances provide a useful first-order view of inputs and outputs associated with in-lake processing of Hg. Such an averaged overview or budget provides a working biogeochemical framework for experimental design, and an important means for scaling and comparing one lake with another on a local or regional basis. Results for the investigated lakes (except Toolik) show that the annual evasional fluxes estimated from an ice-free summertime period (ca. 2 months) for the lakes investigated are quite significant, yielding an average of $7 \pm 3 \text{ nmol m}^{-2} \text{ yr}^{-1}$. These values are comparable to the average annual Hg deposition of $6 \pm 2 \text{ nmol m}^{-2} \text{ yr}^{-1}$ (wet plus dry), estimated from measurements made during July and August 2000 at our atmospheric study site near Toolik Lake. Dry deposition ($\sim 0.5 \text{ nmol m}^{-2} \text{ yr}^{-1}$), calculated by multiplying an estimated particulate Hg concentration of 2 pg m^{-3} with an assumed deposition velocity of 0.15 cm sec^{-1} , is a small portion ($<10\%$) of direct atmospheric input to the lakes. Particulate Hg concentration was estimated from the observed and nearly ideal washout curve of total Hg in the rain ($r^2 = 0.95$, $n = 10$, $p < 0.0001$; inverse power function). We note that this annual total atmospheric Hg depositional flux estimate does not include potentially enhanced Hg inputs that would be associated with unique meteorological conditions and atmospheric chemistry, such as springtime depletion and deposition of atmospheric Hg at high latitudes associated with polar sunrise (Schroeder et al., 1998; Lindberg et al., 2000, 2002). Other contributions from possible vapor phase dry deposition may be considered small relative to the inputs from springtime Hg depletion.

In the case of Toolik Lake, evasional fluxes of $14 \pm 5 \text{ nmol m}^{-2} \text{ yr}^{-1}$ appear to be 2 times greater than the total Hg deposition. Thus, an additional Hg supply (e.g., inputs from point sources, watershed and ground waters etc.) is needed to sustain this level of evasion in Toolik Lake.

3.5. Implication of Estimated Formation Rate of Hg^0 in Surface Lakewaters

The distribution of DGM in water was controlled principally by a combination of physical and biochemical processes (i.e., the rate of formation, oxidation, evasion and mixing). Prior observations show that the rate of Hg^0 oxidation is much smaller in freshwaters than in seawater (Amyot et al., 1994). Therefore, once DGM is produced from photoreduction of Hg(II) -organic complexes in surface waters, it is subsequently mixed and evaded through volatilization after a build-up of DGM at the air-water interface. Thus, assuming that the rate of change of DGM is governed mainly by net production (i.e., a difference between gross production and oxidation of Hg^0) and evasion in a well-mixed layer, we have the following simplified relationship:

$$d[\text{DGM}]/dt = k_f \times [\text{DLM}] - \text{Flux}_{\text{Hg}^0}/D_{\text{ML}} \quad (6)$$

where the term " k_f " refers to the rate constant for net production. The term " D_{ML} " represents the depth of a lake's mixed layer. Sinks of Hg^0 to other reservoirs (e.g., particle scavenging and outflowing water) were ignored because they are assumed to be small relative to the overall gas evasion from lake. If

steady state is assumed, then the net rate of Hg^0_{D} formation should be equal to the evasion rate:

$$k_f \times [\text{DLM}] - \text{Flux}_{\text{Hg}^0}/D_{\text{ML}} = 0 \quad (7)$$

Thus K_f can be described by

$$k_f = \text{Flux}_{(\text{Hg}^0)}/(D_{\text{ML}} \times [\text{DLM}]) \quad (8)$$

In our Arctic lake study, integrated rate constants ranged from 0.02 to 0.05 d^{-1} (i.e., 2 to 6 $\times 10^{-7} \text{ s}^{-1}$). Such values for k_f are comparable to those found in other lacustrine and marine systems (coastal and open ocean), varying from 0.5 to 10 $\times 10^{-7} \text{ s}^{-1}$ (Vandal et al., 1991; Mason et al., 1993a,b, 1994, 1995; Baeyens and Leemakers, 1998; Rolffhus, 1998; Rolffhus and Fitzgerald, 2001). Moreover, daily formation concentrations ranged between 0.02 and 0.10 pM d^{-1} , estimated by multiplying the integrated rate constants with the labile organic complexes-Hg concentration. The integrated production rate, calculated as percent DTM converted to Hg^0 per day, yielded a range of 0.3 to 0.8% d^{-1} with 0.6 ± 0.2 on average.

In summary, the rate at which DGM is produced in Arctic lakes during the ice-free period is affected by both physical and biogeochemical factors. DGM formation shows a weak linear relation with increasing water temperature ($r^2 = 0.55$, $p = 0.02$, $n = 9$). The apparent activation energy (E_a , kJ mol^{-1}) of DGM production was calculated as $150 \pm 40 \text{ kJ mol}^{-1}$ for water temperatures between 11 and 15°C. This value was obtained using the Arrhenius equation ($\ln k_f = \ln A - E_a/RT$) and determining the slope of a linear regression of natural logarithm of formation rate constant versus $1/T$ (Kotz and Purcell, 1987), where k_f is the formation rate constant of Hg^0 and E_a is the activation energy. The activation energy is similar to that estimated for surface waters in Swedish temperate lakes ($\sim 125 \pm 5 \text{ kJ mol}^{-1}$ at water temperatures of 0.5–23°C; Xiao et al., 1991). The estimated formation rate for DGM is slightly diminished with increasing SPM ($r^2 = 0.5$, $p = 0.02$, $n = 9$; data not shown). Finally and most importantly, DOC influences DGM formation in contrasting ways. In low organic carbon regimes, increasing DOC concentrations increase Hg complexation with organic ligands that results in enhanced in situ reduction of Hg(II) . Beyond an optimum DOC concentration (Hg titration), further increases in organic ligands serve only to decrease light availability without enhancing complexation and the specific rate and extent of Hg reduction decreases.

4. CONCLUSION

Lake DGM levels and supersaturation were highest in the near surface photoactive zone. This suggests photoreduction contributes significantly to the speciation and cycling of Hg in terms of Hg^0 production and evasion to the atmosphere. In addition, Hg reduction was mediated by labile photoreducible Hg complexes (presumably organic) in dissolved and particulate phases. Hg reduction proceeds at higher rates in waters with moderate DOC, higher temperature, and lower SPM. DOC can affect the Hg photoreduction by 1) providing a source of reducing agents for Hg reduction when exposed to light, 2) controlling the abundance of photoactive Hg species (e.g., sequestration), and 3) acting as a competitive inhibitor of Hg^0 photoproduction by absorbing solar radiation (i.e., diminishing light availability). However, the effect of DOC as either pro-

motor or inhibitor in Hg^0 production relies on the amount and nature of DOC, the local photo-period, and available sunlight in natural waters.

Knowledge concerning processes and mechanisms of Hg production and their relationships to DOC in aquatic systems is still limited. In particular, organic Hg-binding ligands remain poorly characterized, and photoreducible Hg(II) complexes have been neither identified nor quantified. In addition, the importance of photobiological reduction (e.g., bacterial activity as a source of reducing equivalents) can't be excluded. Mason et al. (1995), for example, suggested that microorganisms ($<3 \mu\text{m}$) were the principal mediators of Hg^0 production in temperate lakes. Amyot et al. (1997a) reported that Hg^0 formation declined by ca. 25% in 0.7 μm filtered water versus unfiltered water in one comparison experiment for North Lake in their Arctic lakes study. While the latter study and our results suggests that the major source of reducing equivalents is related to the amount and composition of the DOC, the role of microorganisms in the aquatic cycling of Hg^0 (fresh an marine) should be carefully quantified and assessed.

Acknowledgments—Logistical support was provided by Veco Polar Resources. We are indebted to Kristin Scott, helicopter coordinator/“problem solver,” Marty Stauber and Dave Mason, pilots, and Don Gregory, mechanic. We thank J. Hobbie N. Bettez, J. Laundre and Kate O'Brien, MBL Ecosystems Center, Woods Hole, Mike Abels, UAF-Alaska Fairbanks, Mike Kleven, BLM, A. Hershey, UNC-Greensboro, G. Kling, UMICH and S. McIntyre, UC Santa Barbara for on/off site assistance. We appreciate the opportunity to use the Toolik Lake LTER facilities. The able support of R. Flanders, station manager, and E. Keltgen were most beneficial. Kelly Thommes of SCWRS conducted the DOC analyses. We were assisted by P. Balcom and C. Hammerschmidt, “Team Mercury,” and Marine Sciences staff, especially our machinists, Gary Grenier and Bob Dziomba. S. Lyons provided editorial assistance with this manuscript. C. Hammerschmidt, Jonathan Kim, Robert Byrne and three anonymous reviewers provided helpful criticisms of the manuscript. This work was funded by NSF-OPP (National Science Foundation-Office of Polar Programs) grant 9908895. This is contribution 316 from the UConn-MSTC (Marine Sciences and Technology Center).

Associate editor: R. H. Byrne

REFERENCES

- Alberts J. J., Schindler J. E., Miller R. W., and Nutter D. E. Jr. (1974) Elemental mercury evolution mediated by humic acid. *Science* **184**, 895–897.
- Allard B. and Arsenie I. (1991) Abiotic reduction of mercury by humic substances in aquatic system—An important process for the mercury cycle. *Water Air Soil Pollut.* **56**, 457–464.
- Amyot M., Mierle G., and Lean D. R. S. (1994) Sunlight-induced formation of dissolved gaseous mercury in lake waters. *Environ. Sci. Technol.* **28**, 2366–2371.
- Amyot M., Lean D. R. S., and Mierle G. (1997a) Photochemical formation of volatile mercury in high arctic lakes. *Environ. Toxicol. Chem.* **16**, 2054–2063.
- Amyot M., Mierle G., Lean D. R. S., and McQueen D. J. (1997b) Effect of solar radiation on the formation of dissolved gaseous mercury in temperate lakes. *Geochim. Cosmochim. Acta* **61**, 975–987.
- Amyot M., Lean D. R. S., Poissant L., and Doyon M.-R. (2000) Distribution and transformation of elemental mercury in the St. Lawrence River and lake Ontario. *Can. J. Fish. Aquat. Sci.* **57**, (Suppl. 1), 155–163.
- Baeyens W. and Leemakers M. (1998) Elemental mercury concentrations and formation rates in the Scheldt estuary and the North Sea. *Mar. Chem.* **60**, 257–266.

- Barkay T., Liebert C., and Gillman M. (1989) Environmental significance of the potential for mer-mediated reduction of Hg^{2+} to Hg^0 in natural waters. *Appl. Environ. Microbiol.* **55**, 1196–1202.
- Ben-Bassat D. and Mayer A. M. (1977) Reduction of mercury chloride by *Chlorella*: Evidence for a reducing factor. *Physiol. Plant.* **40**, 157–162.
- Ben-Bassat D. and Mayer A. M. (1978) Light-induced volatilization and O_2 evolution in *Chlorella* and the effect of DCMU and methylamine. *Physiol. Plant.* **42**, 33–38.
- Benoit J. M., Mason R. P., Gilmour C. C., and Aiken G. R. (2001) Constants for mercury binding by dissolved organic matter isolates from the Florida Everglades. *Geochim. Cosmochim. Acta* **65**, 4445–4451.
- Bloom N. S. (1994) Influence of analytical conditions on the observed “reactive mercury” concentrations in natural freshwaters. In *Mercury Pollution: Integration and Synthesis* (eds. C. J. Watras and J. Huckabee), pp. 541–552. Lewis.
- Bloom N. S. and Crecelius E. A. (1983) Determination of mercury in seawater at sub-nanogram per liter levels. *Mar. Chem.* **14**, 49–59.
- Bloom N. S. and Fitzgerald W. F. (1988) Determination of volatile mercury species at the picogram level by low temperature gas chromatography with cold vapor atomic fluorescence detection. *Anal. Chim. Acta* **208**, 151–161.
- Brown J. and Kreig R. A. (1983) Guidebook to permafrost and related features along the Elliott and Dalton Highway, Fox to Prudhoe Bay, Alaska. In *Proceedings of the 4th International Conference on Permafrost*, July 18–22, 1983, University of Alaska, Fairbanks, 230 pp.
- Brosset C. and Lord E. (1991) Mercury in precipitation and ambient air: A new scenario. *Water Air Soil Pollut.* **56**, 493–506.
- Costa M. and Liss P. S. (1999) Photoreduction of mercury in sea water and its possible implications for Hg^0 air-sea fluxes. *Mar. Chem.* **68**, 87–95.
- Costa M. and Liss P. S. (2000) Photoreduction and evolution of mercury from seawater. *Sci. Total Environ.* **261**, 125–135.
- Dyrssen D. and Wedborg M. (1991) The sulphur-mercury(II) system in natural waters. *Water Air Soil Poll.* **56**, 507–519.
- Fitzgerald W. F. (1999) Clean hands, dirty hands: Clair Patterson and the aquatic biogeochemistry of mercury. In *Clean Hands: Clair Patterson's Crusade Against Environmental Lead Contamination* (ed. C. I. Davidson), pp. 119–137. Nova Science.
- Fitzgerald W. F. and Gill G. A. (1979) Subnanogram determination of mercury by two-stage gold amalgamation applied to atmospheric analysis. *Anal. Chem.* **51**, 1714–1720.
- Fitzgerald W. F., Gill G. A. and Hewitt A. D. (1981) Mercury: A trace atmospheric gas. In: *Proceedings of the 3rd Symposium on the Role of the Ocean in Atmospheric Chemistry*. IAMAP. 3rd Scientific Assembly, Hamburg, 17–28, August.
- Fitzgerald W. F., Gill G. A., and Kim J. P. (1984) An equatorial Pacific Ocean source of atmospheric mercury. *Science* **224**, 597–599.
- Fitzgerald W. F., Vandal G. M., and Mason R. P. (1991) Atmospheric cycling and air-water exchange of Hg over mid-continental lacustrine regions. *Water Air Soil Poll.* **56**, 745–767.
- Fitzgerald W. F., Mason R. P., Vandal G. M., and Dulac F. (1994) Air-water cycling of mercury in lakes. In *Mercury Pollution: Integration and Synthesis* (eds. C. J. Watras and J. Huckabee), pp. 203–220. Lewis.
- Fitzgerald W. F., Vandal G. M., Rolffhus K. R., Lamborg C. H., and Langer C. S. (2000) Mercury emissions and cycling in the coastal zone. *J. Environ. Sci.* **12**, 92–101.
- Gårdfeldt K., Feng X., Sommar J., and Lindqvist O. (2001) Total gaseous mercury exchange between air and water at river and sea surfaces in Swedish coastal regions. *Atmos. Environ.* **35**, 3027–3038.
- Gill G. A. and Fitzgerald W. F. (1985) Mercury sampling of open ocean waters at the picomolar level. *Deep-Sea Res.* **32**, 287–297.
- Hermanson M. H. (1998) Anthropogenic mercury deposition to Arctic lake sediments. *Water Air Soil Poll.* **101**, 309–321.
- Hobbie J. E. (1973) Arctic limnology: A review. In *Alaska Arctic Tundra* (ed. M. E. Britton), pp. 127–168. Technical Paper 25 Arctic Institute North America, **25**, 127–168.
- Hobbie J. E. (1984) Polar limnology. In *Lakes and Reservoirs* (ed. F. B. Taub), pp. 63–105. Elsevier.
- Ji G., Salzberg S. P., and Silver S. (1989) Cell-free mercury volatilization activity from three marine *Caulobacter* strains. *Appl. Environ. Microbiol.* **55**, 523–525.
- Kim J. P. and Fitzgerald W. F. (1986) Sea-air partitioning of mercury in the equatorial Pacific Ocean. *Science* **231**, 1131–1133.
- Kling G. W., O'Brien W. J., Miller M. C., and Hershey A. E. (1992) The biogeochemistry and zoogeography of lakes and rivers in arctic Alaska. *Hydrobiologia* **240**, 1–14.
- Kling G. W., Kipphut G. W., Miller M. M., and O'Briens W. J. (2000) Integration of lakes and streams in a landscape perspective: The importance of material processing on spatial patterns and temporal coherence. *Freshwater Biol.* **43**, 477–497.
- Kotz J. C. and Purcell K. F. (1987) *Chemistry and Chemical Reactivity*. Holt, Rinehart, and Winston.
- Lamborg C. H., Rolffhus K. R., Fitzgerald W. F., and Kim G. (1999) The atmospheric cycling and air-sea exchange of mercury species in the South and equatorial Atlantic ocean. *Deep-Sea Res II* **46**, 957–977.
- Lamborg C. H., Tseng C. M., Fitzgerald W. F., Balcom P. H. and Hammerschmidt C. R. (2003) Determination of the mercury complexation characteristics of dissolved organic matter in natural waters through “reducible Hg” titrations. *Environ. Sci. Technol.* **37**, 3316–3322.
- Larson R. A. and Marley K. A. (1994) Oxidative mechanisms of phototoxicity. *Adv. Environ. Sci. Technol.* **28**, 269–317.
- Landers D. H., Ford J., Gubala C., Monetti M., Lasorsa B. K., and Martinson J. (1995) Mercury in vegetation and lake sediments from the U.S. Arctic. *Water Air Soil Pollut.* **80**, 591–601.
- Lindberg S. E., Brooks S., Lin C.-J., Meyers T. P. and Chambers L. (2000) A preliminary description of recent measurements of mercury depletion events at point Barrow, Alaska. In *Proceedings of the 25th International Conference on Heavy Metals in the Environment*, Ann Arbor, MI, USA. August 6–10.
- Lindberg S. E., Brooks S., Lin C.-J., Scott K. J., Landis M. S., Stevens R. K., Goodsite M., and Richter A. (2002) Dynamic oxidation of gaseous mercury in the Arctic troposphere at polar sunrise. *Environ. Sci. Technol.* **36**, 1245–1256.
- Liss P. S. and Slater P. G. (1974) Flux gases across the air-sea interface. *Nature* **247**, 181–184.
- Lockhart W. L., Wilkinson P., Billeck B. N., Hunt R. V., Wagemann R., and Brunskill G. J. (1995) Current and historical inputs of mercury to high-latitude lakes in Canada and to Hudson Bay. *Water Air Soil Pollut.* **80**, 603–610.
- Mantoura R. F. C., Dickson A., and Riley J. P. (1978) The complexation of metals with humic materials in natural waters. *Estuar. Coastal Shelf Sci.* **6**, 387–408.
- Mason R. P., Fitzgerald W. F., Hurley J., Hanson A. K., Donaghay J. P. L., and Sieburth J. M. (1993a) Mercury biogeochemical cycling in a stratified estuary. *Limnol. Oceanogr.* **38**, 1227–1241.
- Mason R. P. and Fitzgerald W. F. (1993b) The distribution and biogeochemical cycling of mercury in the equatorial Pacific Ocean. *Deep-Sea Res.* **40**, 1897–1924.
- Mason R. P., O'Donnell J., and Fitzgerald W. F. (1994) Elemental mercury cycling within the mixed layer of the equatorial Pacific Ocean. In *Mercury Pollution: Integration and Synthesis* (eds. C. J. Watras and J. Huckabee), pp. 83–97. Lewis.
- Mason R. P., Morel F. M. M., and Hemond H. F. (1995) The role of microorganisms in elemental mercury formation in natural waters. *Water Air Soil Pollut.* **80**, 775–787.
- Mason R. P. and Sullivan K. A. (1997) Mercury in Lake Michigan. *Environ. Sci. Technol.* **31**, 942–947.
- Mason R. P., Lawson N. M., Lawrence A. L., Leaner J. J., Lee J. G., and Sheu G. R. (1999) Mercury in the Chesapeake bay. *Mar. Chem.* **65**, 77–96.
- Mason R. P., Lawson N. M., Lawrence A. L., and Sheu G.-R. (2001) Mercury in the Atlantic Ocean: Factors controlling air-sea exchange of mercury and its distribution in the upper waters. *Deep-Sea Res. II* **48**, 2829–2853.
- Matthiessen A. (1996) Kinetic aspects of the reduction of mercury ions by humic substances: I. Experimental design. Fresenius. *J. Anal. Chem.* **354**, 747–749.

- Miller M. C., Hater G. R., Spatt P., Westlake P., and Yeakel D. (1986) Primary production and its control in Toolik Lake, Alaska. *Hydrobiol. Suppl.* **74**, 97–131.
- Morris D. P., et al. (1995) The attenuation of solar UV radiation in lakes and the role of dissolved organic carbon. *Limnol. Oceanogr.* **40**, 1381–1391.
- Munthe J., Xiao Z. F., and Lindqvist O. (1991) The aqueous reduction of bivalent mercury by sulfide. *Water Air Soil Pollut.* **56**, 621–630.
- Nriagu J. O. (1994) Mechanistic steps in the photoreduction of mercury in natural waters. *Sci. Total Environ.* **154**, 1–8.
- Pehkonen S. O. and Lin C.-J. (1998) Aqueous photochemistry of mercury in natural waters. *J. Air Waste Manage. Assoc.* **48**, 144–150.
- Poissant L., Amyot M., Pilote M., and Lean D. (2000) Mercury water-air exchange over the upper St. Lawrence River and Lake Ontario. *Environ. Sci. Technol.* **34**, 3069–3078.
- Rolfhus K. R. (1998) The production and distribution of elemental Hg in a coastal marine environment. Ph.D. dissertation. University of Connecticut.
- Rolfhus K. R. and Fitzgerald W. F. (2001) The evasion and spatial/temporal distribution of mercury species in Long Island Sound. *Geochim. Cosmochim. Acta* **65**, 407–418.
- Sanemasa I. (1975) The solubility of elemental mercury vapor in water. *Bull. Jpn. Chem. Soc.* **48**, 1795–1798.
- Schroeder W. H., Lindqvist O., Munthe J., and Xiao Z. (1992) Volatilization of mercury from lake surfaces. *Sci. Total Environ.* **125**, 47–66.
- Schroeder W. H., Anlauf K. G., and Barrie L. A. (1998) Arctic springtime depletion of mercury. *Nature* **394**, 331–332.
- Scully N. M. and Lean D. R. S. (1994) The attenuation of ultraviolet light in temperate lakes. *Ergeb. Limnol.* **43**, 135–144.
- Stromberg D., Stromberg A., and Wahlgren U. (1991) Relative quantum calculation on some mercury sulfide molecules. *Water Air Soil Pollut.* **56**, 681–6895.
- Stumm W. and Morgan J. J. (1995) *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*. Wiley.
- Swain E. B., Engstrom D. R., Brigham M. E., Henning T. A., and Brezonik P. L. (1992) Increasing rates of atmospheric mercury deposition in midcontinental North America. *Science* **257**, 784–787.
- Tseng C. M., de Diego A., Martin F. M., and Donard O. F. X. (1997) Rapid and quantitative microwave-assisted recovery of methylmercury from standard reference sediments. *J. Anal. Atom. Spectro.* **12**, 629–635.
- Tseng C. M., Amouroux D., Abril G., Donard O. F. X., Tessier E., and Etcheber H. (2001) Speciation of mercury in a fluid mud profile of a highly turbid macrotidal estuary (Gironde, France). *Environ. Sci. Technol.* **35**, 2627–2633.
- Tseng C. M., Balcom P., Lamborg C., and Fitzgerald W. F. (2003) Dissolved elemental mercury investigations in Long Island Sound using on-line Au amalgamation-flow injection analysis. *Environ. Sci. Technol.* **37**, 1183–1188.
- Vandal G. M., Mason R. P., and Fitzgerald W. F. (1991) Cycling of volatile mercury in temperate lakes. *Water Air Soil Pollut.* **56**, 791–803.
- Vandal G. M., Fitzgerald W. F., Rolfhus K. R., and Lamborg C. H. (1995) Modeling the element mercury cycle in Pallette Lake, Wisconsin, USA. *Water Air Soil Pollut.* **80**, 529–538.
- Wanninkhof R., Ledwell J. R., and Broecker W. S. (1985) Gas exchange-wind speed relationship measured with sulfur hexafluoride on a lake. *Science* **227**, 1224–1226.
- Xiao Z. F., Munthe J., Schroeder W. H., and Lindqvist O. (1991) Vertical fluxes of volatile mercury over forest soil and lake surface in Sweden. *Tellus* **43B**, 267–279.
- Xiao Z. F., Stromberg D., and Lindqvist O. (1995) Influence of humic substances on photolysis of divalent mercury in aqueous solution. *Water Air Soil Pollut.* **80**, 789–798.
- Zhang H. and Lindberg S. E. (2001) Sunlight and iron(III)-induced photochemical production of dissolved gaseous mercury in freshwater. *Environ. Sci. Technol.* **35**, 928–935.